Multiple Charge States of Ag Atoms on Ultrathin NaCl Films

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A combined study using density functional calculations and scanning tunneling microscopy experiments shows that individual silver adatoms on ultrathin sodium chloride films on copper surfaces are stable in three different charge states—neutral, negatively, and positively charged adatoms. The charge states of the individual adatoms were manipulated by voltage pulses. The key parameters determining the stability of various charge states are identified and discussed within a simple model.

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Recent progress in scanning tunneling microscopy (STM) experiments of adsorbates on ultrathin, insulating films has opened up a new field in atomic-scale science. A unique feature of these films is the reduction of the coupling of adsorbate electronic states with the metal support, which enabled the manipulation of electronic [1,2], magnetic [3,4], and conducting [5,6] properties of single adsorbates. A most interesting observation was the charge bistability of individual Au atoms on NaCl films [2] and the ability to switch controllably between these two different charge states. Recently, singly and doubly charged vacancies have been identified in ultrathin MgO films supported by an Ag substrate [7]. The existence and manipulation of multiple charge states of single adatoms will be important for the control of the current in molecular-scale memories and electronics [8]. Moreover, the study of these charging phenomena on an atomic level has ramifications for our understanding of local polaron formation, electron transfer, and electron solvation [9] in a condensed environment, as well as for catalysis on supported metal atom clusters [10].

So far, the observation and manipulation of different charge states of adsorbed atoms have been limited to Au atoms on NaCl films supported by a Cu substrate [2]. On ultrathin MgO films supported by a Mo substrate, density functional calculations suggested that Au adatoms should be spontaneously negatively charged [11]. Thus, it is important to clarify whether the charge multistability of adatoms is unique for the Au/NaCl/Cu system and limited to bistability. Furthermore, one needs to identify the key physical parameters behind this phenomenon.

In this Letter, we show from a combined STM and density functional calculations study that Ag atoms adsorbed on NaCl bilayers on Cu(100) exhibit charge tristability and can be switched reversibly between the neutral adatom state and the negatively or the positively charged adatom state. Thus, the charge multistability of adatoms is not at all unique for Au adatoms, and it is even possible to have more than two different charge states of an adatom. Furthermore, based on a simple model, we identify and discuss the key adatom, film, and substrate parameters for the stabilization of multiple charge states. This model can be used as a guide to find other systems of interest.

The experiments were carried out with a home-built low-temperature STM operated at 5 K. NaCl was evaporated thermally onto clean copper single-crystals having (111), (100), and (311) surface orientations. Ag atoms were deposited inside the STM at a sample temperature below 10 K. For the charge state switching experiments, we positioned the tip on top of an Ag adatom, retracted the tip by up to 8 Å, and applied a voltage pulse of different polarities with the feedback loop turned off. Here, all bias voltages refer to the sample voltage with respect to the tip so that a positive and a negative pulse corresponds to electron and hole tunneling from the tip to the sample, respectively. In the following, the notation A^q refers to an adatom A with charge qe adsorbed on a NaCl film. The data refers to a bilayer NaCl(2ML)/Cu(100), except where stated otherwise. The charge state of an Ag adatom was identified from (1) manipulation of the charge state by electron or hole tunneling, (2) characteristic STM images of the adatom, and (3) the observed behavior of adatom scattering of interface-state electrons on NaCl(2ML)/Cu(111).

Upon deposition, Ag atoms adsorb in a neutral adatom state Ag^0. As shown in Fig. 1, the image of Ag^0 is characterized by a wide featureless protrusion of about 2.5 Å in height. A further analysis of the images, as detailed below, reveals that Ag^0 always adsorbs on top of a Cl anion. However, all these adsorption sites are not equivalent because of the formation of Moiré patterns by the slight lattice mismatch between the NaCl film and the Cu(100) surface [12].

Similarly to the Au adatom charge manipulation [2], Ag^0 can be switched to a negatively charged adatom state Ag^- by electron tunneling ($V \gtrsim 1.3$ V [13]). As for an Au

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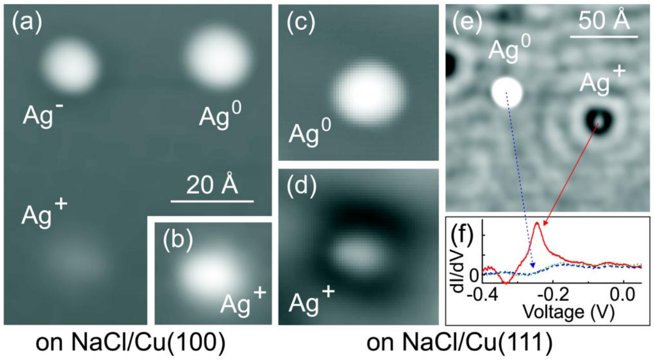

FIG. 1 (color online). STM images and spectra of different Ag adatom states (Ag^0, Ag^+, and Ag^-) on NaCl(2ML)/Cu(100) ((a) and (b)) and Cu(111) ((c) to (f)). In (a) and (c), the maximum scale (white) corresponds to a height of 2.5 Å; (b) and (d) show Ag^+ with the contrast being 4× higher. An image at even higher contrast (e) and local dI/dV spectra (f) show scattering of interface-state electrons and an interface-state localization at Ag^+ but not at Ag^0. The solid, dashed, and dotted spectrum refers to Ag^+, Ag^0 and bare NaCl/Cu, respectively. The bias and the tunneling currents are (a) 50 mV, 1 pA; (b) 200 mV, 0.5 pA; (c) −558 mV, 62 pA; (d) −211 mV, 62 pA; (e) 15 mV, 0.8 pA.

adatom, the formation of Ag^- results in both a sudden drop in the current signal by about a factor of 3 and an image that is characterized by a 2.0-Å-high protrusion, surrounded by a faint depression (sombrero shape). The switching is also reversible, that is, Ag^- can be transformed back into Ag^0 by hole tunneling ($V \lesssim -0.2$ V [13]). Note that because of the Moiré pattern, Ag^- is unstable for some sites and will switch back to Ag^0 spontaneously before Ag^- can be imaged. On a trilayer NaCl(3ML)/Cu(100), this spontaneous neutralization always occurs.

In contrast to an Au adatom, an Ag adatom can also be manipulated to a positively charged adatom state Ag^+ by hole tunneling ($V \lesssim -1.3$ V [13]). This manipulation is possible for all adsorption positions of Ag^0 with respect to the Moiré pattern and results in a stable Ag^+. The images of an Ag^+ is characterized by a small protrusion of only about 0.5 Å in height and having an elongated shape. By electron tunneling ($V \gtrsim 1.5$ V [13]), Ag^+ can again be neutralized but also be desorbed.

The adsorption sites of Ag^0, Ag^- and Ag^+ were determined experimentally from the STM images. In atomically resolved images [14–16], Ag^+ was found at a site bridging two Cl anions with its protrusion being elongated towards the two nearest neighboring Cl anions. Using the Ag^+ as a marker, the adsorption sites of Ag^- and Ag^0 were both found to be on top of the Cl anions.

To provide further justification of our assignment of the charge states of the different Ag adatom states, we employed a recently developed scheme [5] based on the observed behavior of the interaction of interface-state (IS) electrons of NaCl/Cu(111) with the Ag adatoms. On this surface, the Ag adatoms exhibit a similar switching behavior as on NaCl/Cu(100) except that Ag^- is not stable, which we attribute to the larger work function of NaCl/Cu(111). The identification of a localized IS in the dI/dV spectrum (Fig. 1(f)) at Ag^+ shows that it is positively charged [17,18]. In the case of Ag^0, both the absence of a localized IS and a much weaker standing-wave pattern of IS electrons than from Ag^+ are consistent with Ag^0 being neutral (Figs. 1(e) and 1(f)). Finally, the similarities of the manipulation procedure and STM images of Ag^- to Au^- [2] indicate that Ag^- is negatively charged.

To gain physical insight into the nature of Ag adatom states on NaCl(2ML)/Cu(100), we have carried out periodic density functional theory calculations of their geometric and electronic structure and energetics, using the VASP code [19,20]. The electron-ion core interactions were treated by the projector augmented wave method [21,22]. The electron exchange-correlation interactions were treated by a generalized gradient approximation (GGA) [23]. To avoid an unphysical fractional occupation of the Ag^0 as is introduced by an underestimate of the integer discontinuities of the chemical potential in the GGA [24], we included also an on-site Coulomb repulsion $U = 1.6$ eV (GGA + U) [25] in an s projector of the Ag atom. The value of U was chosen to reproduce the proper discontinuity of the free atom, as determined by its calculated affinity and ionization energies [26].

In our calculations, we have identified three different charge states of the Ag adatoms—Ag^0, Ag^+, and Ag^-—that are (meta-)stable and exhibit the same characteristics as Ag^0, Ag^+, and Ag^- in the experiments. The adsorption site on top of the Cl anion is found to be the most stable site for the neutral Ag^0 [27,28] and the negatively charged Ag^-, whereas the adsorption site bridging two Cl anions is the most stable site for the positively charged Ag^+. Ag^+ and Ag^0 were both found to be weakly bonded to the surface, with adsorption energies (E_a) of 0.30 and 0.11 eV, respectively. Despite its small negative E_a of about −0.01 eV, the Ag^- state is metastable owing to the formation of an energy barrier for desorption by the ionic relaxations as discussed below.

In our calculations, Ag^+ on top of a Na cation is only slightly less stable ($E_a = 0.26$ eV) than Ag^+ in bridge position. The ionic relaxations pattern is similar to the one induced by Ag^- when interchanging the Na cations and Cl anions in the film. This adsorption state of Ag^+ has not been found in the experiment. It could be that Ag^+ in bridge position is favored as a result of the trajectory in the switching of Ag^0 on top of the Cl site to a positively charged state. In the following, we will only refer to the bridge Ag^+ adsorption state.

The bonding of the Ag^- and Ag^+ to the NaCl film is qualitatively different from each other, as indicated by their different adsorption geometries. The Ag^+ has a short Ag-Cl bond length of 2.3 Å and is adsorbed only 0.5 Å outside the nearest neighboring Cl anions, which have a large

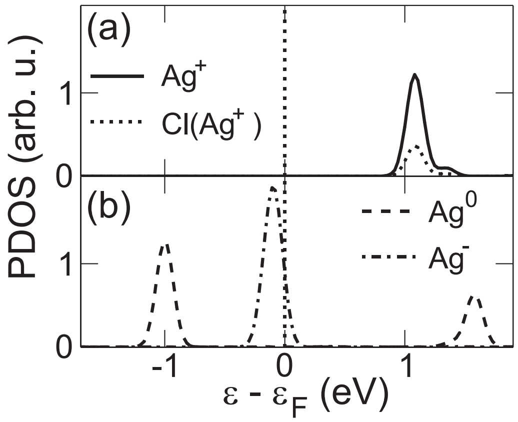

FIG. 2. Calculated PDOS around Ag^0, Ag^+ and Ag^- on NaCl(2ML)/Cu(100). (a) PDOS of s- and p-waves around Ag^+ and its nearest neighboring Cl atom, respectively. (b) PDOS of s-waves around Ag^0 and Ag^-. For Ag^0 an on-site Coulomb repulsion of $U = 1.6$ eV and spin polarization were used. Note that the broadening of PDOS is artificial and its intrinsic broadening cannot be resolved in these calculations.

outward relaxation by 0.5 Å. Ag^-, on the other hand, has a large Ag-Cl interatomic distance of 3.5 Å and induces large relaxations in the NaCl film: an outward and inward relaxation of about 0.6 Å of the nearest neighboring Na cations and Cl anions, respectively. This relaxation pattern is similar to the one induced by the Au^- adatom on top of an Cl anion. In contrast to the charged adatom states, the neutral Ag^0 does not induce any significant relaxations of the Na cations and Cl anions, and adsorbs at a large Ag-Cl interatomic distance of about 3.0 Å.

The charge states of Ag^0, Ag^+, and Ag^- and the nature of the adatom-film bond are revealed by the calculated partial density of states (PDOS) (Fig. 2) and also by electron density rearrangements upon adsorption (Fig. 3). The PDOS of s-waves around the Ag adatom shows that the state derived from the singly occupied 5s-orbital of the free Ag atom is fully occupied for the Ag^-, singly occupied for the Ag^0, and unoccupied for Ag^+. These findings corroborate our previous experimental assignment of the charge states of the Ag adatoms. The PDOS around the Ag^+ adatom and the nearest neighboring Cl anion also exhibit some mixing of Ag s-states with Cl p-states corresponding to a depopulation of antibonding Ag-Cl states and the formation of a $[AgCl_2]^-$ complex with a covalent character of the bonding of the Ag^+ and Cl^- ions. This depopulation shows up as an accumulation of electron density between the Ag adatom and the nearest neighboring Cl anions (Fig. 3(a)). In contrast, the electron density difference for the Ag^- (Fig. 3(c)) only shows a large electron accumulation around the adatom and the formation of an ionic bond.

The physical mechanism behind the stabilization of various charged adatom states is the formation of an energy barrier between an adatom with charge $qe = \pm e$ and the neutral adatom by ionic relaxations in the film (Fig. 4). This diabatic picture is similar to the classical Marcus picture for electron transfer [29]. A necessary condition for the existence of such an energy barrier is the condition that the energy costs $\Delta E(0 \rightarrow q)$ and $\Delta E(q \rightarrow 0)$ for charging the neutral adatom A^0 and neutralizing the charged adatom A^q at fixed equilibrium ionic configurations, respectively, both be positive. The key parameters determining these energies are most easily identified by assuming that the ionic and the electronic response of the film and the metal substrate are linear to the charging of the adatom. Under this assumption, the charge-switching energy-barriers are given by

$$\Delta E(0 \rightarrow q) = \begin{cases} \Phi - A - \Delta E_{\mathrm{el}}, & \text{for } q = -1 \\ I - \Phi - \Delta E_{\mathrm{el}}, & \text{for } q = +1 \end{cases}, \tag{1}$$

$$\Delta E(q \rightarrow 0) = 2\Delta E_{\mathrm{ion}} - \Delta E(0 \rightarrow q), \tag{2}$$

where A and I are the affinity and ionization energies of the free atom, respectively, and ΔE_{el} and ΔE_{ion} are the electronic relaxation and ionic reorganization energies gained by charging the atom, respectively, and Φ is the work function of the surface. A large ΔE_{ion} favor the stabilization of A^q and is obtained whenever the static dielectric constant is substantially larger than the optical one for the film.

There is a delicate balance between the other key parameters A, I, Φ, and ΔE_{el} for the stability of the various

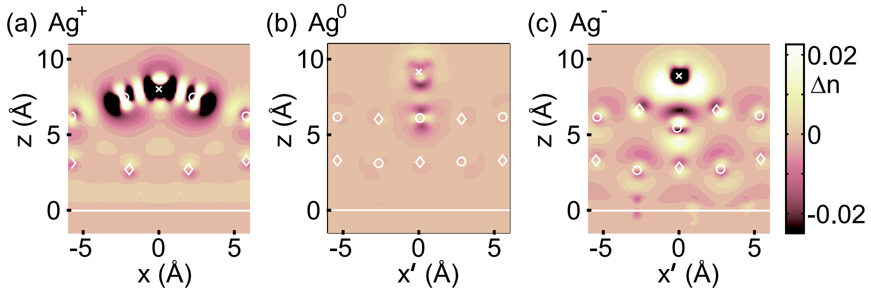

FIG. 3 (color online). Cross section of the calculated electron density differences, Δn, of (a) Ag^+, (b) Ag^0, and (c) Ag^-. $\Delta n = n_{\mathrm{Ag+substr}} - n_{\mathrm{Ag}} - n_{\mathrm{substr}}$, given in units of $e/\text{Å}^3$. The positions of the Ag atoms, Na, and Cl ions are represented by crosses, diamonds, and circles, respectively. The Cu(100) surface plane is indicated by a solid line. x and x' are the coordinates along the [011] (a) and [100] (b, c) direction of the NaCl film, respectively.

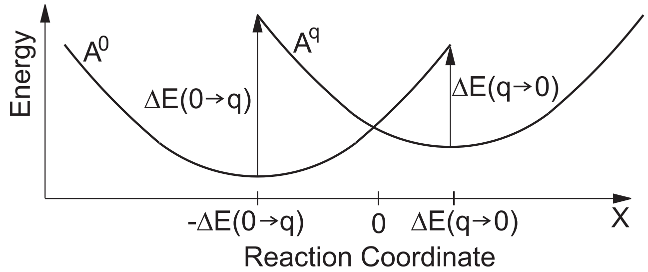

FIG. 4. Schematic energy diagram for the stabilization of a neutral adatom state A^0 and charged adatom state A^q with charge qe by ionic relaxation in a linear response model. The two diabatic potential energy curves, Marcus parabolas, are the minimum potential energies of A^0 and A^q with respect to ionic configurations that are constrained to have a fixed value for the reaction coordinate X, defined as the potential energy difference between A^0 and A^q. $\Delta E(0 \longrightarrow q)$ and $\Delta E(q \longrightarrow 0)$ are the energy costs for charging A^0 and neutralizing A^q at fixed ionic equilibrium configurations, respectively.

charged adatom states. A unique feature of Au is its large value of 2.3 eV for A, which favors the stabilization of Au^-, but the relatively small value of 1.3 eV for A of Ag shows that it is not a necessary condition for a stable negatively charged adatom state. However, this relatively small value for A of Ag makes Ag^- marginally stable: the increase of Φ for NaCl(2ML)/Cu(111) compared with that for NaCl(2ML)/Cu(100) and the decreasing electronic polarization from the metal substrate to ΔE_{el} for increasing number of layers make Ag^- unstable on NaCl(2ML)/Cu(111) and NaCl(3ML)/Cu(100), respectively. Furthermore, the relatively small value for Φ of about 2.8 eV for NaCl(2ML)/Cu(311) tends to stabilize A^-. In fact, only Au^- was identified on NaCl/Cu(311). The formation of Ag^+ is favored by its relatively small value for $I = 7.6$ eV compared with $I = 9.2$ eV for Au.

In conclusion, from scanning tunneling microscopy measurements and density functional theory calculations of Ag adatoms on NaCl bilayers supported by a Cu surface, we have demonstrated that charge multistability and the atomic-scale control of the charge state of adsorbates are not limited to Au adatoms and to bistability but that also tristability is possible. The key parameters behind the charge multistability are identified and suggest that it should be a common phenomenon, with important ramifications for molecular-scale electronics and memories.

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